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Evolution of Long Period Stacking Order structures on annealing As-Cast  $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$  Alloy Ingot  
Observed by Synchrotron Radiation Small-Angle Scattering.

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Abstract: Nanostructure of  $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$  ternary alloy ingot with long-period stacking order structure has been examined by synchrotron radiation small-angle X-ray scattering. The scattering patterns showed sharp reflections corresponding to large domains of 10H, 18R and 14H structures, with in-plane ordering. After annealing at 673 K, the peak intensity of 18R increased, and the diffraction peak corresponding to in-plane ordering sharpened. The domain size of in-plane ordering was much smaller than the domain thickness of 18R in the stacking direction.

(abstract 78 words)

Key Words,

LPSO; Mg alloys; small-angle scattering; in-plane ordering; 10H;

Strong light-weight structure materials are one of the key technologies for green society. In 2001, Kawamura et al. [1,2] found a series of interesting Mg-based light alloys containing very small amount of rare earth (RE) elements and transition metals (TM), possessing excellent mechanical properties. The phase responsible for the strengthening of the alloy has a long period ordered structure in the direction parallel to the *c* axis of the matrix hcp Mg, with periodical stacking fault and segregation structures as made clear by high resolution electron microscopic works[3-7]. So far, 10H, 14H, 18R and 24R structures have been reported[3-8], and these phases are called Long Period Stacking Order structure (LPSO). Yokobayashi et al. [8] found that an annealed MgGdAl ternary alloy gave a well-defined long period stacking order and an in-plane order structure, and explained the whole structure in terms of Order-Disorder structure[9,10], which in turn assumes full ordering in the in-plane direction. On the other hand, many LPSO-Mg alloys found so far showing well-defined layer structure such as 14H or 18R, do not necessarily exhibit such clear in-plane ordering in electron micrographs, although the ones shown by Egusa et al.[11] for well-annealed  $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$  alloy showed weak but clear in-plane ordering.

Examining relative stability among several LPSO structures with different periodicities, and the effect of in-plane ordering on the sequence of LPSO phase during casting and subsequent annealing and deformation is important to understand the mechanism how and why such structures appear by the heat treatment. It is important not only for the basic understanding from a view point of phase transformation, but also from a practical reason that phase diagram for such alloy systems giving complicated and time-dependent phases is hard to determine but requisite for practical materials design. Recent work by Grobner et al[12] examined a phase diagram for LPSO and related phases in Mg rich corner of the ternary alloys, which suggested stable region for 18R and 14H, and their coexistence region. They also suggested slightly different composition for 14H and 18R. However,

there are some experimental results that are not fully explained by the diagram. Also, the role of in-plane ordering is not fully understood in relation to the phase stability in the alloys. To understand the role of in-plane ordering in forming such peculiar LPSO phase, it is important to use an approach that evaluates the microstructure from a macroscopic region and has a potential to lead to in-situ experiments. In the present work, we performed synchrotron-radiation small-angle X-ray scattering (SR-SAXS) measurements on one of the representative LPSO-forming alloys, i.e., polycrystalline  $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$  cast alloys, and obtained a development of well defined scattering from both the LPSO structures and in-plane ordering during annealing at 673 K. The SAXS measurements were performed at Beam-Line 6A of Photon Factory, Tsukuba Japan with a photon energy of 8.2 keV[13] Cooled CCD with Image Intensifier (II-CCD) was used for the present measurements with exposure between 0.2 s and 6 s.

Figure 1 shows a schematic illustration of LPSO structures for 18R reported by preceding researchers[3-8]. It contains three stacking faults at every 6 atomic layers, accompanying 4 segregation layers with enrichment of Zn and Y in c direction. The in-plane ordering model proposed by Yokobayashi et al. [8] consists of  $\text{RE}_8\text{TM}_6\text{L}_{12}$  cluster units regularly aligned in the segregation layers with hexagonal symmetry, which stabilize the stacking fault at the segregation layers. Since small-angle scattering is sensitive to the compositional modulation but not sensitive to the stacking fault, SAXS profile concerning the LPSO structure simply represents the compositional periodicity of every 6 layers for 18R structures, and every 5 layers if the LPSO structure is 10H. We may hereafter call them 6N and 5N for simplicity. To add with, a diffraction peak may appear if in-plane ordering develops. In the present work, the scattering vector range from  $1.0\text{ nm}^{-1}$  to  $9.0\text{ nm}^{-1}$  was measured simultaneously by an II-CCD detector, intended to cover up to the second peaks of LPSO diffraction.

Figure 2 gives a two-dimensional SAXS profile shown in a logarithmic intensity scale. It is seen

that there are two kinds of scattering patterns in the figure. Sharp spots aligning in two Debye rings represent first order diffraction peaks for 6N (inner circle) and 5N (outer circle). Several spots corresponding to 7N (14H) were also observed. The diffraction spots on the rings are sharp and are separated each other along the rings, meaning that diffractions from individual grains are recorded. As encircled in the figure, there are several pairs of spots that a 6N spot and a 5N spot are aligned on the same radial direction and connected by a streak, suggesting that 18R and 10H structures coexist in a coherent way in the same grains, as for the case of intergrowth during cooling the ingot. The diffraction profiles of each spot at the 6N and 5N rings, both in radial (thickness) and tangential in-plane) directions, suggest that the peaks are as sharp as the resolution limit of the present SAXS camera, about 50 nm. Therefore, it is concluded that both 18R and 10H structures have well defined thick domains already well developed in the as-cast state, and in a coherent manner.

Figure 3 shows the relative change of the integrated intensity of the first 6N peak upon annealing at 673 K. The profile was radially averaged and normalized by the first peak of 5N. The 6N peak gradually increased with time. Considering the microstructure observation by microscope that Mg solid solution ( $\alpha$ ) grain is not clearly observed and the volume fraction of LPSO structure is close to 100% for the present condition, this indicates that the 18R grew at the cost of 10H structure. On the other hand, rather sluggish decrease of 10H peak during annealing suggests that the 18R domain thickness grew because of relative stability over 10H, i.e., 673 K is not the order/disorder temperature for the 10H structure where 10H structure collapse.

Another remarkable feature in Fig.2 is six-fold diffuse spots outside the two Debye rings of 5N and 6N LPSO diffraction. The peak positions of the spots are  $|q_m|=5.87 \text{ nm}^{-1}$ , giving the lattice spacing of 1.07 nm. This spacing is close to that for the in-plane order structure reported for MgGdAl alloys by Yokobayashi et al[8]. However, the in-plane ordering spots observed in the present work are very diffuse as compared with the well-defined 6N and 5N LPSO diffraction spots. This result suggests

that the in-plane ordering remains in small domains. A simplest approach to evaluate the domain size is to consider a two-dimensional Laue function of the superstructure lattice spacings, whose magnitude is  $2\sqrt{3}$  times the matrix Mg lattice[8]. The FWHM of the diffuse spot,  $\Delta q$ , is then related to the domain size by

$$D = 2\pi / \Delta q \quad (1)$$

The FWHM of the peak was  $2.35 \text{ nm}^{-1}$  in the present measurements, corresponding to the domain size of 2.7 nm. It suggests that an average two-dimensional order domain contains about 7 or 8  $L1_2$  cluster units. Although the domain size is larger than the segregation periodicity of 1.8 nm for 6N, it is of the same order of magnitude as the lattice constant in the c direction for 18R, 4.7 nm and much smaller than the domain thickness of LPSO grain, which is larger than 50 nm. Therefore, from the order spot profile, it is concluded that the in-plane ordering in the present as-cast  $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$  alloy is rather under a medium-range order (MRO) stage.

Figure 4 gives the change of the peak position and the FWHM of the in-plane order spot. The figure shows that the FWHM of the in-plane order spot decreases from  $2.35 \text{ nm}^{-1}$  to  $1.1 \text{ nm}^{-1}$ , corresponding to the increase in the size of in-plane order domain from 2.7 nm to 5.7 nm. The average distance between the  $L1_2$  clusters slightly decreases during annealing at 673 K. There are two possible explanations for the change of the in-plane superstructure lattice constant. One is that fully ordered structure has smaller lattice parameters, which is elongated when embedded in disordered LPSO region. The other is that coexisting 10H and 18R have different in-plane lattice parameters, thereby increase of volume fraction of 18R changes the in-plane lattice parameters. From the present results showing no clear lattice parameter change for 18R(6N) with annealing time, the former explanation seems feasible, but further examination using a single crystal is necessary to reach a conclusion. For LPSO diffraction spots corresponding 6N and 5N periodicities, more than 50 grains appeared on the two dimensional scattering pattern, while the 6-fold pattern should be

apparently attributed to a single grain. In the present work, measured profiles suggested that the number of the grains that gave in-plane ordering peak was mostly one or two, less than four. Two-fold pattern for the in-plane order spot was not observed in the present measurements. This result might be qualitatively explained by the texture and the solid angle effect that the solid angle allowed to give a diffraction spot on the Debye rings, i.e.,  $c$  axis is in-plane to the detector, is much larger than the solid angle allowed to give a 6-fold pattern, i.e., the  $c$  axis is normal to the detector surface, provided that allowance for the diffraction condition is almost the same. Since the condition also strongly depends on the texture, and is hard to determine which grain to satisfy the diffraction condition, quantitative analysis on the degree of order is difficult at this moment. However, considering the fact that preparing a large single crystal is very difficult for this alloy system, and that the LPSO phase appearing in the two-phase condition where  $\alpha$  Mg solid solution and LPSO phase coexist is important for practical use, present SAXS approach is useful to understand the relative stability of LPSO structures having different periodicities, and the role of in-plane ordering in such structures.

To summarize, we demonstrate SAXS results which clearly show well-defined LPSO structure having large 10H and 18R domains. The coexistence of the 10H and 18R in the same grain and their relative stability with annealing at 673 K was also shown. In-plane ordering with relatively small domain size was observed as a 6-fold scattering pattern, suggesting that the ordering occurs uniformly but with small order domain size. Whether the in-plane order structure in MgYZn develop to form fully ordered one as described by Order-Disorder structure [8-10] or essentially remain in short-to-medium range order, i.e., LPSO structure but not OD structure, will be made clear by examining the temporal evolution of the scattering / diffraction patterns. In-situ time-resolved SAXS measurements for isothermally annealed samples are now under progress.

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Figure captions

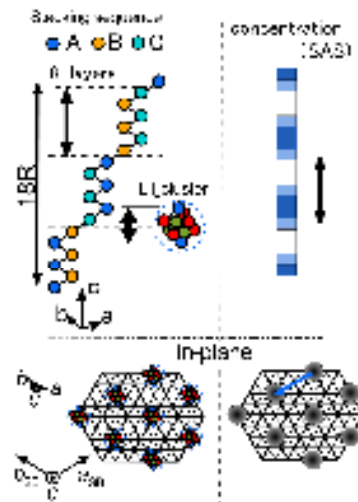


Figure 1.

Schematic illustration of 18R structure proposed by Matsuda et al.[3] with a proposed in-plane ordering structure suggested by Yokobayashi et al.[8]. Since the SAXS reflects components normal to the stacking fault, the pattern for LPSO periodicity reflects the periodic composition modulations as schematically shown in the right column of the figure.

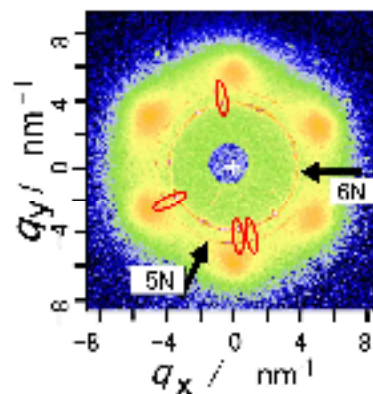


Figure 2.

SAXS pattern obtained for the present sample. It is clearly seen that two Debye rings corresponding

to 5N and 6N stacking periodicity indicating diffraction from stacking sequence and 6-fold diffuse scattering corresponding to the in-plane ordering overlapping on a measured pattern.

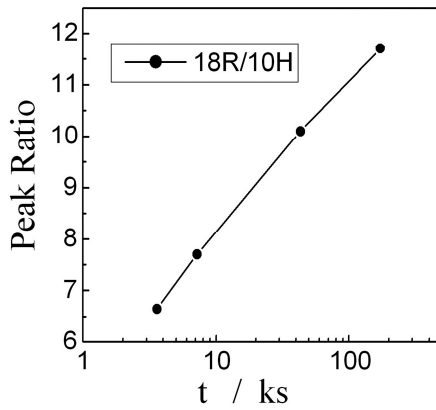
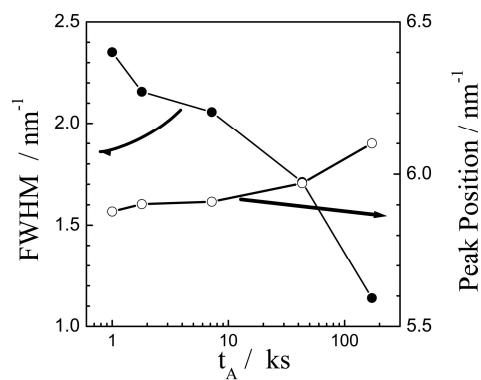


Figure 3.

Change of the integrated intensity of the first 18R peak relative to that of 10H peaks obtained from circularly averaged SAXS patterns during annealing at 673K.

Figure 4.



FWHM and the peak position of the first in-plane order spots. The peak increases and sharpens by annealing, and the peak position moves slightly to larger  $q$ , i.e., smaller in-plane lattice constants for ordering.